



PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of:

Taizou ITOU, et al

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For: METHOD FOR MEASURING WATER CONCENTRATION IN AMMONIA

SUBMISSION OF SWORN TRANSLATION OF PROVISIONAL APPLICATION

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

Pursuant to 37 C.F.R. §1.78(a)(5), submitted herewith is a sworn English language translation of the provisional application upon which a claim for benefit is based.

Respectfully submitted,

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DECLARATION

I, Atsuko Ikeda, residing at 26-2-906, Ojima 3-chome, Koto-ku, Tokyo, Japan, do hereby certify that I am conversant with the English and Japanese languages and am a competent translator thereof. I further certify that to the best of my knowledge and belief the attached English translation is a true and correct translation made by me of U.S. Provisional Patent Application No. 60/176,799 filed on January 19, 2000.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 4th day of April, 2000

Atsuko Ikeda

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[NAME OF DOCUMENT] Specification

[TITLE OF THE INVENTION]

Method for Measuring Water Concentration in Ammonia

[SCOPE OF CLAIM FOR PATENT]

[Claim 1] A method for measuring a water concentration in ammonia using infrared spectrometry, wherein the measurement uses a wave number in the range of from 4,000 to 3,500 cm^{-1} , from 3,100 to 2,600 cm^{-1} , or from 2,400 to 1,900 cm^{-1} .

[Claim 2] The method for measuring a water concentration in ammonia as claimed in claim 1, wherein said measurement wave number is one or more selected from the group consisting of 3600, 3609, 3612, 3619, 3629, 3634, 3649, 3656, 3670, 3675, 3688, 3691, 3701, 3709, 3712, 3719, 3722, 2727, 3732, 3736, 3741, 3744, 3749, 3752, 3756, 3759, 3766, 3770, 3779, 3785, 3796, 3801, 3807, 3816, 3821, 3826, 3831, 3835, 3837, 3840, 3843, 3854, 3862, 3865, 3870, 3874, 3880, 3885, 3891, 3894, 3899, 3902 and 3904 cm^{-1} (variation width: $\pm 1 \text{ cm}^{-1}$).

[Claim 3] The method for measuring a water concentration in ammonia as claimed in claim 1 or 2, wherein said measurement wave number is one or more selected from the group consisting of 3801, 3807, 3816, 3821, 3837 and 3854 cm^{-1} (variation width: $\pm 1 \text{ cm}^{-1}$).

[Claim 4] The method for measuring a water

concentration in ammonia as claimed in any one of claims 1 to 3, wherein said ammonia is obtained by vaporizing liquefied ammonia.

[Claim 5] The method for measuring a water concentration in ammonia as claimed in any one of claims 1 to 4, wherein said ammonia has a water concentration of 10 ppm or less.

[Claim 6] The method for measuring a water concentration in ammonia as claimed in any one of claims 1 to 5, wherein ammonia gas is introduced into a multi-reflection long optical path cell.

[Claim 7] The method for measuring a water concentration in ammonia as claimed in any one of claims 1 to 6, wherein ammonia gas is introduced into said multi-reflection long optical path cell at a flow rate of from 0.1 to 5 L/min.

[Claim 8] The method for measuring a water concentration in ammonia as claimed in any one of claims 1 to 7, wherein an infrared ray is multi-reflected to have an infrared optical path length of from 1 to 40 m.

[Claim 9] The method for measuring a water concentration in ammonia as claimed in any one of claims 1 to 8, wherein the gaseous phase moiety of liquefied ammonia having a water concentration of 10 ppm or less is used as a reference gas.

[Claim 10] An infrared measuring apparatus comprising an infrared spectroscope, a long optical path gas cell, a flow rate controlling unit and a vaporizer, wherein ammonia gas vaporized by the vaporizer is fed into the flow rate controlling unit, the ammonia gas is introduced from the flow rate controlling unit into the long optical gas cell at a constant flow rate, and the water content of ammonia in the long optical path gas cell is measured by the infrared spectroscope.

[Claim 11] The infrared measuring apparatus as claimed in claim 10, wherein said long optical path gas cell has a volume of from 0.1 to 5 L.

[Claim 12] The infrared measuring apparatus as claimed in claim 10 or 11, wherein ammonia gas is introduced into the long optical path gas cell at a flow rate of from 0.1 to 5 L/min controlled by said flow rate controlling unit.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Technical Field to Which the Invention Belongs]

The present invention relates to a method for measuring a water concentration in ammonia using infrared spectrometry, particularly, a concentration of trace water contained in high-purity ammonia used as a raw material in the production of a semiconductor, for example, a GaN-type

compound semiconductor, and an infrared measuring apparatus using the method.

[0002]

[Background Art]

It is known that the water content of a raw material gas used in the production of a semiconductor greatly affects the device characteristics. In particular, for the production of a GaN crystal which is one of the blue light emitting devices, ammonia having a low water concentration is necessary. In order to measure the water concentration in ammonia, various methods have heretofore been proposed and particularly for measuring water content in a low concentration in ammonia, (1) gas chromatography (GC method), (2) thermal decomposition dew point method, (3) laser spectrometry and (4) infrared spectrometry are known.

[0003]

JP-A-9-142833 (the term "JP-A" as used herein means an "unexamined published Japanese patent application") discloses a method of reacting water in ammonia with calcium carbide as a reacting agent and detecting the acetylene generated by GC method. This method has a problem in that not only the water content but also organic impurities in the calcium carbide reacted are detected and to avoid this, high-purity and stabilized calcium carbide is necessary but this is hardly available at present. In

addition, the GC method is low in the accuracy and not practical for the analysis in the level of several ppm or less because the system has a switch cock for feeding a sample or a backflash cock for removing ammonia before it enters the detector, and the water adsorption onto the inner surface of pipelines increases.

[0004]

SEMI standard (SEMI C3, 12-94) and JP-A-8-201370 describe a thermal decomposition dew point method. The thermal decomposition dew point method is a method of decomposing ammonia into nitrogen and hydrogen at a high temperature near 1,000°C using an Ni catalyst or a noble metal catalyst, and measuring the water content by a dew-point instrument. According to this method, oxygen in the gas reacts with hydrogen to produce water and the water content may be excessively determined. Not only oxygen is contained in the raw material gas but also an oxide of the catalyst or pipeline material exposed to high temperatures may cause hydrogen reduction to produce water. Therefore, the reliability for accuracy decreases in the measurement of water content of 1 ppm or less. Moreover, to be dangerous, flammable ammonia is laid in a high temperature environment of 1,000°C or more and safety equipment in a large scale is necessary. Thus, this method is not simple and convenient.

[0005]

Laser spectrometry is described in Proceedings of the 5th International Symposium on Semiconductor Manufacturing (1996, jointly sponsored by UCS/IEEE/SEMI), page 321. In measuring the water absorption in the near infrared region by laser spectrometry, since water is present in the vicinity of the absorption region of ammonia, a wavelength resolving power of high level is necessary but at present the separation cannot be attained due to the interaction between gas molecules. Therefore, ammonia gas reduced in the water content as low as negligible must be used as a reference gas but it has been heretofore difficult to simply prepare high-purity ammonia reduced in the water content, which can be used as the reference gas.

[0006]

The infrared spectrometry has a problem in that the ammonia has a broad absorption band and particularly when a water concentration of 100 ppm or less is measured, the absorption by ammonia and the absorption by water cannot be easily separated because even the weak absorption by ammonia is present near the absorption by water in many cases. Furthermore, similarly to the above-described laser spectrometry, ammonia gas reduced in the water content as low as negligible must be used as a reference gas but this has been heretofore difficult to obtain.

As such, conventionally known methods for measuring a water concentration in ammonia have various problems particularly in the case of measuring the water content in a low concentration in ammonia. Thus, more improvements are demanded.

[0007]

[Problems to be Solved by the Invention]

The present invention has been made under these circumstances and the objects of the present invention are to provide a method for measuring a water concentration in ammonia using infrared spectrometry, which can measure the water content particularly in a low concentration in ammonia, and to provide an infrared measuring apparatus.

[0008]

[Means to Solve the Problems]

As a result of extensive investigations to attain these objects, the present inventors have found that in the method of measuring a water concentration in ammonia using infrared spectrometry, the gaseous phase moiety of liquefied ammonia having a water concentration of 10 ppm or less can be used as a reference gas because the water content is very small. Furthermore, it has been found that the above-described objects can be attained by using a method of introducing an ammonia gas into a multi-reflection long optical path cell at a constant flow rate

and measuring it at a wave number having no overlapping of the infrared absorption by ammonia and the infrared absorption by water, in combination with an infrared measuring apparatus equipped with a vaporizer for vaporizing the liquefied ammonia and a flow rate controlling unit. The present invention has been accomplished based on these findings. The present invention relates to a method for measuring a water concentration in ammonia using infrared spectrometry and an infrared measuring apparatus, described in (1) to (12) below:

[0009]

(1) a method for measuring a water concentration in ammonia using infrared spectrometry, wherein the measurement uses a wave number in the range of from 4,000 to 3,500 cm^{-1} , from 3,100 to 2,600 cm^{-1} , or from 2,400 to 1,900 cm^{-1} :

(2) the method for measuring a water concentration in ammonia as described in (1) above, wherein the measurement wave number is one or more selected from the group consisting of 3600, 3609, 3612, 3619, 3629, 3634, 3649, 3656, 3670, 3675, 3688, 3691, 3701, 3709, 3712, 3719, 3722, 2727, 3732, 3736, 3741, 3744, 3749, 3752, 3756, 3759, 3766, 3770, 3779, 3785, 3796, 3801, 3807, 3816, 3821, 3826, 3831, 3835, 3837, 3840, 3843, 3854, 3862, 3865, 3870, 3874,

3880, 3885, 3891, 3894, 3899, 3902 and 3904 cm^{-1} (variation width: $\pm 1 \text{ cm}^{-1}$);

(3) the method for measuring a water concentration in ammonia as described in (1) or (2) above, wherein the measurement wave number is one or more selected from the group consisting of 3801, 3807, 3816, 3821, 3837 and 3854 cm^{-1} (variation width: $\pm 1 \text{ cm}^{-1}$);

(4) the method for measuring a water concentration in ammonia as described in any one of (1) to (3) above, wherein the ammonia is obtained by gasifying liquefied ammonia;

(5) the method for measuring a water concentration in ammonia as described in any one of (1) to (4) above, wherein the ammonia has a water concentration of 10 ppm or less;

[0010]

(6) the method for measuring a water concentration in ammonia as described in any one of (1) to (5) above, wherein ammonia gas is introduced into a multi-reflection long optical path cell;

(7) the method for measuring a water concentration in ammonia as described in any one of (1) to (6) above, wherein ammonia gas is introduced into the multi-reflection long optical path cell at a flow rate of from 0.1 to 5 L/min;

(8) the method for measuring a water concentration in ammonia as described in any one of (1) to (7) above, wherein the infrared ray is multi-reflected to have an infrared optical path length of from 1 to 40 m;

(9) the method for measuring a water concentration in ammonia as described in any one of (1) to (8) above, wherein the gaseous phase moiety of liquefied ammonia having a water concentration of 10 ppm or less is used as a reference gas;

(10) an infrared measuring apparatus comprising an infrared spectroscope, a long optical path gas cell, a flow rate controlling unit and a vaporizer, wherein ammonia gas gasified by the vaporizer is fed into the flow rate controlling unit, the ammonia gas is introduced from the flow rate controlling unit into the long optical gas cell at a constant flow rate, and the water content of ammonia in the long optical path gas cell is measured by the infrared spectroscope;

(11) the infrared measuring apparatus as described in (10) above, wherein the long optical path gas cell has a volume of from 0.1 to 5 L; and

(12) the infrared measuring apparatus as described in (10) or (11) above, wherein ammonia gas is introduced into the long optical path gas cell at a flow rate of from 0.1 to 5 L/min by the flow rate controlling unit.

[0011]

In other words, the present invention is a method for measuring a water concentration in ammonia, where the gaseous phase moiety of liquefied ammonia having a water concentration of 10 ppm or less is used as a reference gas, ammonia is introduced into a multi-reflection long optical path cell, and the infrared absorption intensity is measured at a wave number having no overlapping of the infrared absorption by ammonia and the infrared absorption by water, and also is an infrared measuring apparatus capable of measuring the water content in both ammonia gas and liquefied ammonia, which is equipped with a vaporizer having a function of controlling the temperature and a flow rate controlling unit for introducing a gas into a gas cell at a constant flow rate.

[0012]

[Mode for Carrying Out the Invention]

As described above, in the case of measuring the water content in ammonia by infrared spectrometry, ammonia gas having a water content as small as negligible needs be used as a reference gas. To this purpose, the present inventors have measured the gas-liquid partition coefficient of water distributed to the gaseous phase and the liquid phase of liquefied ammonia in a water concentration region of 10 ppm or less by infrared

spectrometry, as a result, this was revealed to be a very small value with gaseous phase concentration/liquid phase concentration being from 0.1 to 0.01. Heretofore, no paper has reported on the gas-liquid partition coefficient of liquefied ammonia in a water concentration region of 10 ppm or less. However, from the result above, it has been found that the gaseous phase of ammonia having a very low liquid phase water concentration is ammonia gas reduced in the water content as low as negligible and can be used as the reference gas in the infrared spectrometry of the present invention.

[0013]

At this time, the calibration curve used for the determination of a water concentration is obtained by mixing 50% of the above-described ammonia gas having a very low water concentration and 50% of nitrogen having a water concentration of from 0.5 to 2 ppm and determining the correlation between the water concentration and the infrared absorption intensity at a measurement wave number selected from the ranges of from 4,000 to 3,500 cm^{-1} , from 3,100 to 2,600 cm^{-1} , and from 2,400 to 1,900 cm^{-1} . For simply determining the water concentration of ammonia gas, it may also be possible to correct and convert a value obtained from a water concentration calibration curve of nitrogen 100% gas.

[0014]

When the infrared absorption wave number of ammonia and the infrared absorption wave number of water are examined in particular, the infrared absorption wave numbers of water present in the ranges of from 4,000 to 3,500 cm^{-1} , from 3,100 to 2,600 cm^{-1} and from 2,400 to 1,900 cm^{-1} are found to be small in the influence of ammonia and free of overlapping with the infrared absorption by ammonia. Therefore, the infrared absorption intensity is measured using one or more of wave numbers falling within these ranges, preferably one or more wave number selected from the group consisting of 3600, 3609, 3612, 3619, 3629, 3634, 3649, 3656, 3670, 3675, 3688, 3691, 3701, 3709, 3712, 3719, 3722, 2727, 3732, 3736, 3741, 3744, 3749, 3752, 3756, 3759, 3766, 3770, 3779, 3785, 3796, 3801, 3807, 3816, 3821, 3826, 3831, 3835, 3837, 3840, 3843, 3854, 3862, 3865, 3870, 3874, 3880, 3885, 3891, 3894, 3899, 3902 and 3904 cm^{-1} (variation width: $\pm 1 \text{ cm}^{-1}$), more preferably one or more wave number selected from the group consisting of 3801, 3807, 3816, 3821, 3837 and 3854 cm^{-1} (variation width: $\pm 1 \text{ cm}^{-1}$).

[0015]

Ammonia gas is introduced into a multiple reflection long optical path cell and determined on the infrared absorption intensity. The infrared measuring apparatus of the present invention has a vaporization unit, therefore,

can analyze even liquefied ammonia. This is suitably used for the measurement of a trace water concentration of 10 ppm or less in ammonia. At the time of introducing ammonia gas into the multiple reflection long optical path cell, the flow rate of ammonia gas is controlled using a flow rate controlling unit. The flow rate is constant and is suitably from 0.1 to 5 L/min, preferably from 0.5 to 3 L/min. If the flow rate is less than 0.1 L/min, reproducibility of the measurement results cannot be obtained, whereas if the flow rate exceeds 5 L/min, the ammonia gas disadvantageously contaminates the measurement environment. The infrared ray is multi-reflected so as to increase the sensitivity, and the optical path length here is suitably from 1 to 40 m, preferably from 2 to 30 m, more preferably from 4 to 20 m. With this optical path length, the sensitivity is remarkably improved and good sensitivity can be obtained.

[0016]

The method for measuring a water concentration in ammonia and the infrared measuring apparatus of the present invention are described below by referring to a schematic view of the apparatus shown in Fig. 1.

The apparatus shown in Fig. 1 is an apparatus for infrared spectrometry, equipped with an infrared spectroscope 1, a long optical gas cell 2 for introducing

ammonia gas, a vaporization unit 3 for vaporizing liquefied ammonia, a connecting line 4 for connecting a measurement sample cylinder 9, a connecting line 5 for connecting a reference gas cylinder 10, a water adsorption tube 6 for drying nitrogen used for purging the pipelines, a water adsorption tube 7 for drying nitrogen used for purging the infrared spectroscope, and a flow meter 8.

[0017]

For measuring the water content in ammonia, the measurement sample cylinder 9 and the reference gas cylinder 10 are connected to the connecting line 4 and the connecting line 5, respectively. Dry nitrogen passed through the adsorption tube 6 is allowed to flow through the connecting lines 4 and 5, a flow rate controlling unit 19 shown in Fig. 3 is adjusted to give a constant flow rate in the flow meter 8, and the pipelines are dried for 30 minutes or more.

Subsequently, dry nitrogen is introduced into the long optical path gas cell 2 and the inside of the gas cell 2 is dried to reduce the water content in nitrogen to 1 ppm or less. Thereafter, feeding of dry nitrogen is stopped and then ammonia gas is introduced from the reference gas cylinder into the gas cell 2. At this time, similarly to nitrogen, the flow rate is controlled to a constant flow rate by the flow rate controlling unit 19. The reference

gas is passed for 60 minutes or more and after replacing the gas in the gas cell 2, the infrared absorption spectrum is measured. The results obtained are used as the background of the infrared spectroscope 1.

[0018]

Then, passing of the reference gas is stopped and ammonia gas or liquefied ammonia is allowed to flow from the measurement sample cylinder 9 connected to the connecting line 4. In the case of ammonia gas, the gas flow rate is controlled to a constant flow rate by the flow rate controlling unit 19. In the case of liquefied ammonia, a thermostatic chamber 17 is set at a temperature of from 40 to 150°C and after the liquefied ammonia flowing through the heated vaporizer 18 is vaporized, the gas is controlled to a constant flow rate. In either case, the gas is passed through the gas cell at the same flow rate as in the measurement of the reference gas for 60 minutes or more and after replacing the gas within the gas cell 2, the water absorption intensity is measured.

[0019]

Fig. 3 shows a vaporization unit 3 which is used in the case of measuring the water content of liquefied ammonia. Liquefied ammonia is introduced into the SUS-made vaporizer 18 (diameter: 1/4" to 1/16", length: 0.5 to 5 m) heated at from 40 to 150°C using the thermostatic chamber

17 and after the gasification by heating, the flow rate is controlled by the flow rate controlling unit 19. The gas flow rate is suitably from 0.1 to 5 L/min.

[0020]

Fig. 4 shows the results obtained when two kinds of liquefied ammonia different in the water concentration (1.7 ppm or 0.3 ppm) each is vaporized using the vaporization unit 3 and the ammonia gas is introduced into a gas cell having an optical path length of 10 m at a flow rate of 2 L/min and analyzed with the background of the reference gas. From the results obtained, it is seen that the wave number used in the measurement is preferably $3801 \pm 1 \text{ cm}^{-1}$, $3807 \pm 1 \text{ cm}^{-1}$, $3816 \pm 1 \text{ cm}^{-1}$, $3821 \pm 1 \text{ cm}^{-1}$, $3837 \pm 1 \text{ cm}^{-1}$ or $3854 \pm 1 \text{ cm}^{-1}$.

[0021]

[Effects of the Invention]

As described in the foregoing pages, according to the method and apparatus for measuring a water concentration in ammonia of the present invention, one or more wave number in the ranges of from 4,000 to 3,500 cm^{-1} , from 3,100 to 2,600 cm^{-1} and from 2,400 to 1,900 cm^{-1} is used, so that even in the case of liquefied ammonia, needless to say about ammonia gas, water in a low concentration region of 10 ppm or less can be simply and easily analyzed. Furthermore, removal of water in ammonia or the effect of water concentration on the device characteristics can be

estimated, therefore, productivity in the manufacturing process can be elevated.

[BRIEF DESCRIPTION OF DRAWINGS]

[Fig. 1]

Fig. 1 is a view showing an apparatus for infrared spectrometry for measuring a water concentration in ammonia according to the present invention.

[Fig. 2]

Fig. 2 is a cross-sectional view of the long optical path gas cell shown in Fig. 1.

[Fig. 3]

Fig. 3 is a view showing the vaporization unit shown in Fig. 1.

[Fig. 4]

Fig. 4 is a view showing infrared absorption spectra of water in ammonia measured by the method of the present invention.

[Description of Numerical References]

- 1 infrared spectroscope
- 2 long optical path gas cell
- 3 vaporization unit
- 4, 5 connecting lines
- 6 dryer for pipeline-purging gas
- 7 dryer for infrared spectroscope-purging gas
- 8 flow rate indicator

- 9 measurement sample cylinder
- 10 reference gas cylinder
- 11 infrared ray reflection mirror
- 12 acuminous barrel
- 13 gas inlet valve
- 14 gas outlet valve
- 15 infrared ray entering window
- 16 infrared ray exiting window
- 17 thermostatic chamber
- 18 vaporizer
- 19 flow rate controlling unit

[NAME OF THE DOCUMENT] Abstract

[SUMMARY]

[PROBLEM TO BE SOLVED]

To provide a method and an apparatus for measuring a water concentration in ammonia, which can measure water in a low concentration even if the ammonia is liquefied ammonia, to say nothing about ammonia gas.

[MEANS TO SOLVE THE PROBLEM]

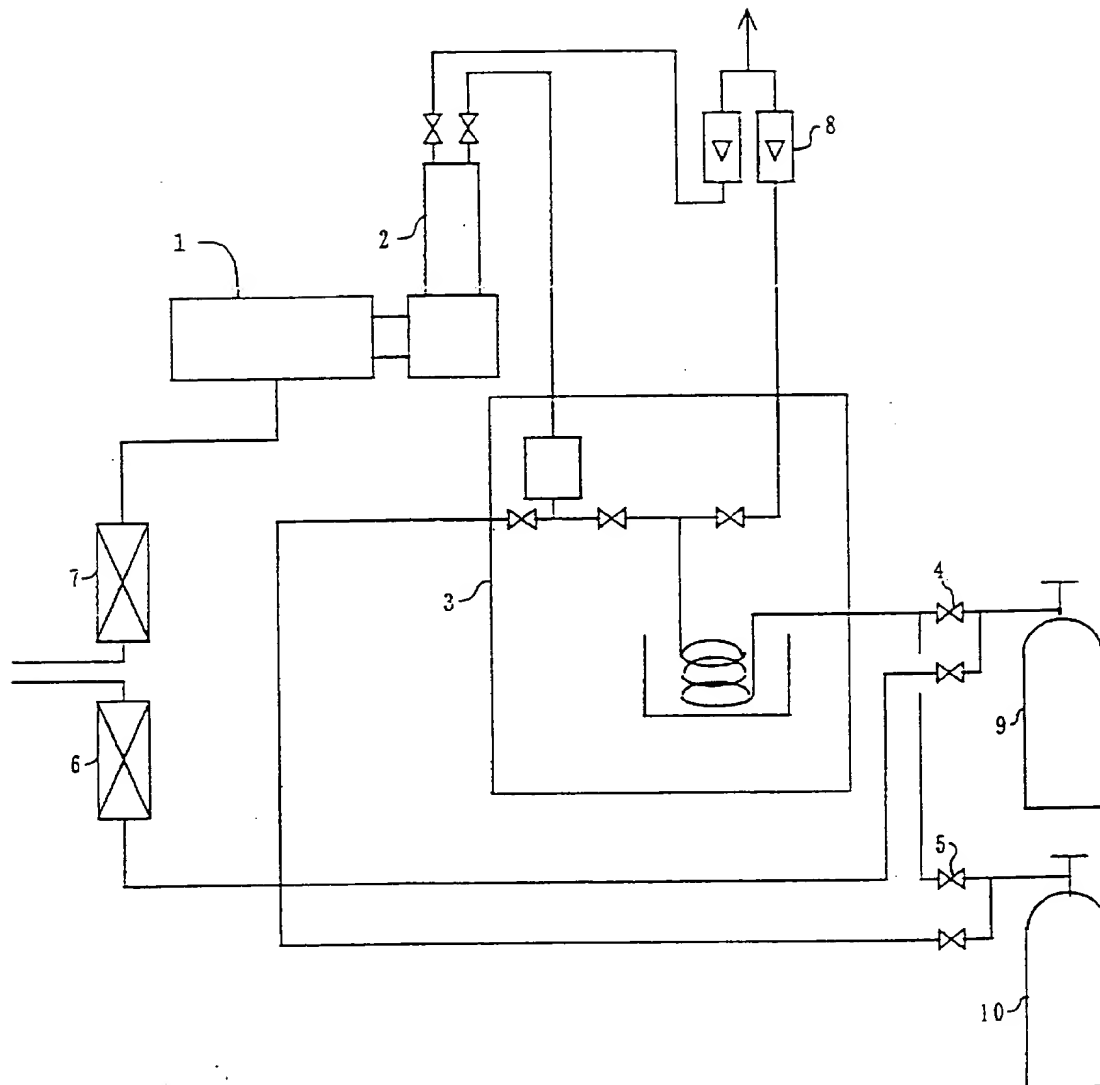
The infrared absorption intensity of water is measured using a measurement wave number in the range of from 4,000 to 3,500 cm^{-1} , from 3,100 to 2,600 cm^{-1} , or from 2,400 to 1,900 cm^{-1} , by introducing ammonia gas into a long optical path gas cell at a constant flow rate and multi-reflecting an infrared ray in the cell.

[SELECTED DRAWING] None.

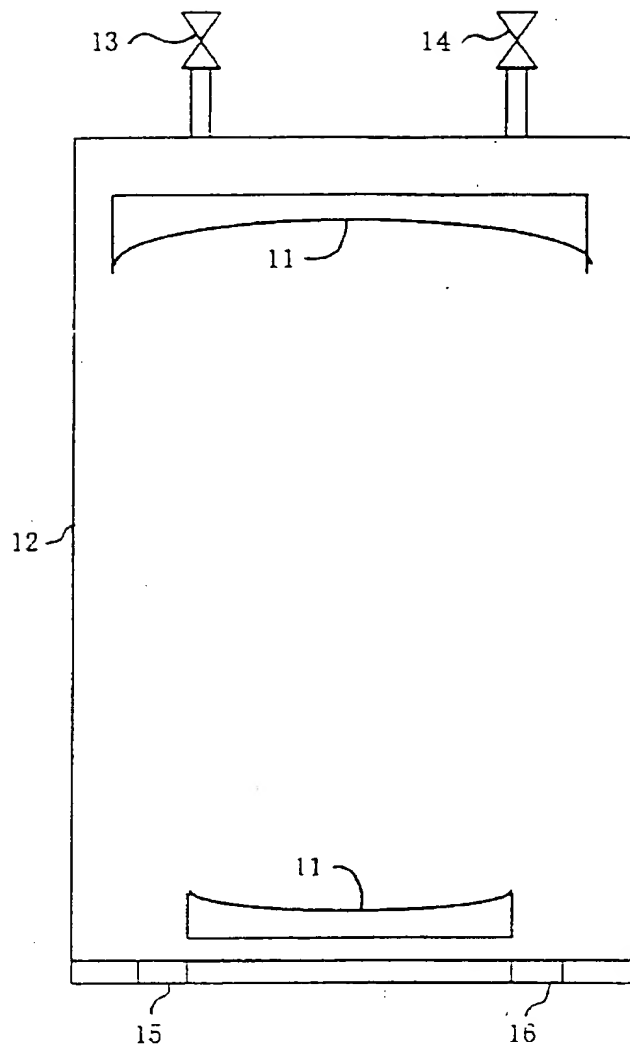
[NAME OF DOCUMENT]

Drawings

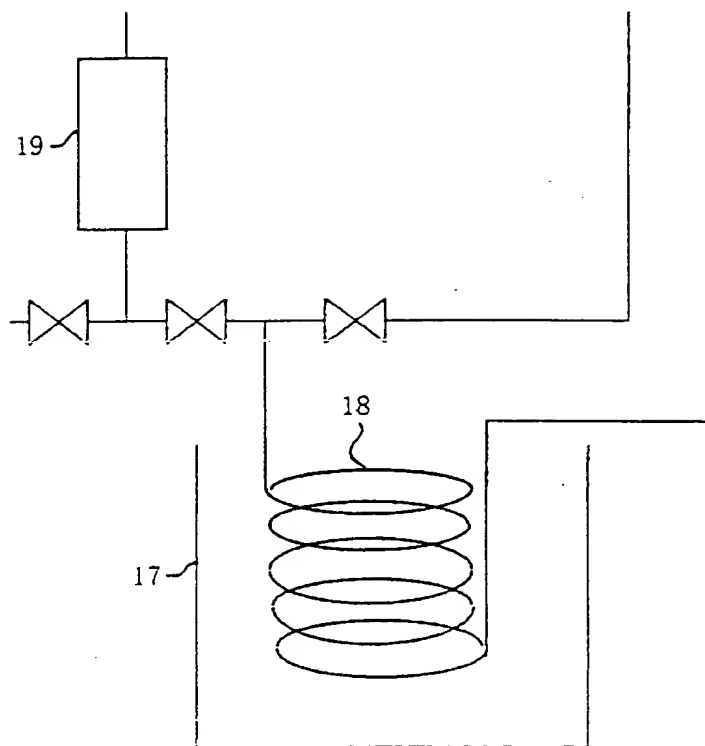
[Fig. 1]



[Fig. 2]



[Fig. 3]



[Fig. 4]

